Running Head:

WOOD CHAR-WATER SORPTION COEFFICIENTS OF ORGANIC SORBATES

Corresponding Author:

Prof. Desiree L. Plata
Yale University
Department of Chemical and Environmental Engineering
9 Hillhouse Ave
PO Box 208286
New Haven CT 06520
203-436-9066 (T)
203-432-4387 (F)
desiree.plata@yale.edu

Polyparameter Linear Free Energy Relationship for Wood Char-Water Sorption Coefficients of Organic Sorbates

Desiree L. Plata[*†§], Jordon D. Hemingway[‡§], and Philip M. Gschwend[§]

[†]Department of Chemical and Environmental Engineering, Yale University, New Haven, CT, USA

[‡]Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, USA

[§]Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA

*Address correspondence to desiree.plata@yale.edu

Abstract

Black carbons (BCs), including soots, chars, activated carbons, and engineered nanocarbons, have different surface properties, but we do not know to what extent these affect their sorbent properties. To evaluate this for an environmentally ubiquitous form of BC, biomass char, we probed the surface of a well-studied wood char using 14 sorbates exhibiting diverse functional groups and then fit the data with a polyparameter linear free energy relationship (ppLFER) to assess the importance of the various possible sorbate-char surface interactions. Sorption from water to water-wet char evolved with the sorbate's degree of surface saturation and depended on only a few sorbate parameters:

$$\log K_d(\mathrm{L/kg}) = [(4.03 \pm 0.14) + (-0.15 \pm 0.04) \log a_i)]\, V + [(-0.28 \pm 0.04) \log a_i)]\, S + (-5.20 \pm 0.21)\, B$$

where a_i is the aqueous saturation of the sorbate *i*, *V* is McGowan's characteristic volume, *S* reflects polarity, and *B* represents the electron-donation basicity. As generally observed for activated carbon, the sorbate's size encouraged sorption from water to the char, while its electron donation/proton acceptance discouraged sorption from water. However, the magnitude and saturation dependence differed significantly from what has been seen for activated carbons, presumably reflecting the unique surface chemistries of these two BC materials and suggesting BC-specific sorption coefficients will yield more accurate assessments of contaminant mobility and bioavailability and evaluation of a site's response to remediation.

Keywords

Sorption, Wood char, Hydrophobic organic compounds (HOCs), Polyparameter linear free energy relationship (ppLFER), Black carbon (BC)

INTRODUCTION

In an effort to manage contaminated sediments and soils, regulators try to use data on solid phase concentrations of organic contaminants to identify deposits that pose unacceptable toxic risks. Commonly, this is done by assuming equilibrium partitioning of the compounds among the solid phases, porewater or soil gas, and associated organisms [1]. The key parameter allowing us to use sediment/soil concentrations in this model is the solid-water sorption coefficient, K_d [(mol/kg_{solid})/(mol/L_{water})]. In the case of contaminated sediments, this allows us to estimate porewater concentrations, C_w, from the ratio, C_{sed}/K_d.

Until now, regulators have assumed that K_d for most nonionic contaminants is given by the product, $f_{oc}K_{oc}$, where f_{oc} is the organic carbon content of the sediment (kg_{oc}/kg_{solid}) and K_{oc} is the organic carbon-normalized solid-water partition coefficient [(mol/kg_{oc})/(mol/L_{water})]. However, such sorption modeling has been found to be extremely inaccurate at many sites [2,3]. If it were accurate, then one should find close correspondence between porewater concentrations and sediment concentrations normalized by $f_{oc}K_{oc}$. Instead, measured values of C_w are commonly up to a *factor of 100* less than $C_{sed}/f_{oc}K_{oc}$ [4]! Likewise, biota-sediment accumulation factors (BSAFs) measured for a wide range of benthic infauna are often 1 to 2 orders of magnitude below the corresponding equilibrium partitioning expectation [5-7]. This situation suggests that there is a major problem with respect to estimating solid-water partition coefficients using only an $f_{oc}K_{oc}$ model.

We now know that sediments and soils include "black carbons" (BCs) such as soots, biomass chars, and coal dust residues, and that these special components of the total organic carbon must be distinguished from the rest of the organic matter to estimate accurately K_d values of many contaminants [8-14]. Thus, sorption estimations can be greatly improved by using an extended expression that includes black carbon as a separate sorbent [10]

$$K_d = f_{oc}K_{oc} + f_{BC}K_{BC}C_w^{(n\text{-}1)} \quad (1)$$

where f_{oc} is now the non-BC organic carbon weight fraction in the sediment, f_{BC} is the BC weight fraction, K_{BC} is the compound specific BC-water adsorption coefficient, and $C_w^{(n\text{-}1)}$ is the dissolved sorbate concentration of compound raised to a power, n-1, to reflect the nonlinearity of adsorption to the BC surface. To date, the majority of available K_{BC} values are derived from studies using engineered, granular activated carbon (GAC) as a sorbent, but distinct BCs may have different sorption coefficients from GAC. If so, then solid-water partitioning models would be improved by the use of the appropriate K_{BC} when the sorbent identity is known (e.g., near a coal storage site or after application of an engineered biochar). In the present study, we explore the sorption parameters for a biochar (K_{char} and n_{char}) for a structurally diverse array of sorbates and compare those to sorption parameters for GAC in order to determine if BC-specific sorption parameters are needed.

Chars, themselves, are ubiquitous and structurally diverse [15] and can have a wide range of surface areas and surface functionalities, depending on the conditions of

their formation [16, 17]. However, chars formed at greater than about 400^{o}C typically have predominantly aromatic surface character [17-19] and some oxygen-containing functionalities [20, 21]. Further, biochars are increasingly investigated as "green" sorbates, as they can be made from waste biomaterials, and they have abundant natural, incidental, and engineered sources globally (Figure 1).

Hence, here we characterize sorption of 14 diverse sorbates to a wood char formed at 450^{o}C . After determining the isotherms, polyparameter linear free energy relationship (ppLFER) modeling was used to identify the most important intermolecular interactions controlling sorption to this water-wet char. The choice of model sorbates was intended to capture the widest degree of variability in the Abraham/McGowan [25, 26] sorbate parameter space with a relatively small number of sorbates that are liquids at room temperature. Overall, our goals were to (a) enable prediction of partitioning coefficients for untested compounds whose parameters fall within our tested range for this particular wood char and (b) add to the understanding of the fundamental mechanisms of sorption from water to unique biochars. We note that applying the resultant ppLFER outside the training set parameter space (e.g., extrapolating to estimate K_{BC} values for PCBs) may result in large errors in estimated K_ds, especially as steric issues related to the sorbates' surface interactions and pore access can arise.

EXPERIMENTAL METHODS

Chemical sorbates.

We used 14 sorbates (Table 1) with varied functional groups, covering a range of the ppLFER parameter space (i.e., *V* from 0.715 to 1.154, *E* from 0 to 0.871, *S* from 0 to 1.11, *A* from 0 to 0.37, and *B* from 0 to 0.51). While these probe compounds do not cover the entire known range of the parameters [25, 26], they do represent diverse intermolecular forces and have a relatively broad range in aqueous solubilities (Table 1). Any ppLFER can only be justifiably applied within the tested Abraham/McGowan parameter space, rather than outside of it (i.e., the V, E, S, A, and B of a compound must fall within the range tested here if the ppLFER is to give accurate results). Sorbate-saturated aqueous solutions were prepared by equilibrating excess quantities of each sorbate with 18MΩ UV-oxidized water for at least 1 wk in pre-combusted, ground-glass-stoppered flasks.

Char sorbent.

Wood char, prepared from chestnut hardwood pyrolyzed at 450^{o}C as described in Hammes et al. [21; see also 27, 28], was purchased from the Schmidt Laboratory at the University of Zurich (Supplemental Data, Table S1). To ensure uniform sorbate exposure to char surfaces and ultimately aid in gravitational settling of the char, the fine char particles were dispersed in ethyl acetate, spread over pre-combusted, acid-washed, Ottawa sand, and then stirred semi-continuously while air drying. The char-quartz mixture was further dried at 60^{o}C for 72 h, with stirring every 12 h. The weight percent carbon contents of the quartz, char, and the char-quartz mixture were 0.016 ± 0.006, 71.7 ± 0.2, and 1.1 ± 0.2 % C, respectively, as determined using a CHN analyzer (Vario EL, Elementar America, Inc.) operated at a combustion temperature of 950 °C. Specific areas

for quartz, char, and the char-quartz mixture were 3.3, 5.9, and 3.6 m^2 g^{-1}, respectively, as determined by single-point nitrogen BET (Brunauer-Emmett-Teller) testing (PMI Analytical Testing, Ithaca, NY). Note that Hammes et al. [21] reported 2.0 m^2 g^{-1} for this particular wood char.

Sorption equilibration experiments.

All batch sorption experiments were conducted in pre-combusted, 7-mL, 18-mL, or 50-mL ground-glass-stoppered centrifuge tubes. All-glass containers were used to avoid sorbate losses to Teflon™ or other polymers [29-31]. Sorbent (i.e., char-quartz mixture) and sorbent-free (i.e., quartz only) samples were pre-wet with 18 MΩ water for at least 1 wk prior to sorbate addition. Serial dilutions of the water-saturated sorbate stocks were gravimetrically prepared (at 0.1, 0.01, 0.001, and 0.0001 aqueous saturation) and then immediately added to triplicate sorbent containers. Headspace was minimized to avoid sorbate loss to the vapor phase. Sorbate concentrations were quantified following 7-to-14 d equilibration times, which we determined was sufficient to establish equilibrium (based on a toluene sorption time-series (Supplemental Data, Figure S1; Table S2). To minimize the influence of suspended colloids on the measured dissolved aqueous concentrations of sorbate, each test tube was centrifuged at 1150 *g* for at least 90 min prior to sorbate quantification. Recall that the char itself was spread over quartz sand (through the use of an ethyl acetate carrier) to ensure uniform exposure of the char and to aid gravitational settling.

As sorption to char is a surface process, we chose to probe the char surface as a function of sorbate *activities*, rather than *concentrations*. Here, recognizing that these

liquid sorbate's solubilities represent 100% saturation in solution, the fractional saturation in solution also corresponds to the same degree of saturation (or chemical activity) on the char surface at solution-surface equilibrium in a batch experiment. This allowed us to investigate the effect of increasing surface coverage between highly variable sorbates. Since the probe sorbates' have a broad range of aqueous solubilities, and comparison at equal concentrations would either unnecessarily limit the range of chemical loadings (i.e., for the most water-soluble species) or result in the formation of a pure sorbate phase (i.e., for the least soluble species), which would confound the results.

Sorbate quantification and sorption calculation.

Analytes with relatively low aqueous solubilities (<6,000 mg/L) were quantified using a purge and trap pre-concentrator (Tekmar LCS 2000) interfaced to a gas chromatograph (GC; Perkin Elmer AutoSystem XL) with a flame ionization detector (FID) for hydrocarbons or an electron capture detector (ECD) for halogenated compounds. Analytes with relatively high aqueous solubilities (>6,000 mg/L) were quantified via direct aqueous injection onto a GC-FID (Carlo Erba HRGC 5300 Mega Series MFG 500). Both instruments were equipped with a DB-624 capillary column (60 m x 3.80 um x 0.320 mm) and temperature programs varied with the analyte.

The average aqueous sorbate concentration in char-free control tubes (i.e., quartz only; n=3) was compared to the aqueous sorbate concentration in char-containing tubes (i.e., C_w), where the difference was attributed to sorption to char. This mass difference was normalized to the mass of char sorbent to give the concentration of sorbate on the solid char (i.e., C_s). For hexane and heptane, which have relatively high air-water

partition coefficients, we also accounted for the mass of sorbate in test tube bubbles that evolved during the course of the equilibration (<1 mL, where the volume was deduced by changes in weight).

Sorption isotherms.

The experimentally-determined C_s and C_w data were fit to the log-transformed Freundlich equation

$$\log C_s = \log K_f + n \log C_w \qquad (2)$$

where C_s and C_w are equilibrium concentrations in the solid phase (mg/kg) and aqueous phase (mg/L), respectively, and K_f [(mg/kg)/(mg/L)^n] and n (dimensionless) are the Freundlich coefficient and Freundlich exponent, respectively.

Polyparameter linear free energy relationship.

All measures of K_d (i.e., *each* C_w/C_s *pair*) were used to evaluate the dependence of K_d on sorbate properties (i.e., the Abraham/McGowan parameters) by fitting the saturation-dependent ppLFER (Eqn. 3).

$$\log K_{d,activity}\,(\text{L/kg}) = (v_1 + v_2 \log a_i)V + (e_1 + e_2 \log a_i)E + (s_1 + s_2 \log a_i)S + (a_1 + a_2 \log a_i)A + (b_1 + b_2 \log a_i)B + c_1 + c_2 \log a_i \qquad (3)$$

where V (in cm^3 mol^{-1}/100) is the sorbate's McGowan characteristic volume, E (in cm^3/10) is the excess molar refraction, S is the polarity/polarizability parameter, A and B are the hydrogen acidity and basicity, respectively, and $a_i = C_{iw}/C_{iw,sat}$, is the ratio of the

sorbate *i*'s concentration to its (liquid) solubility. Coefficients were determined both by backward and forward stepwise multiple linear regression analysis of experimental values using Microsoft™ Excel and StatPlus™. In the case of backward fitting, the significance of each term in equation 3 was evaluated using a *t* test to determine the probability that the coefficient was different from zero. Insignificant terms were systematically eliminated one at a time and then the regression analysis was repeated until only significant correlation coefficients remained (i.e., via backward stepwise multiple regression analysis) and the ANOVA factor, F, was maximized. Given a data set of 128 observations, 6-12 parameters could be fit meaningfully, but we ultimately found only 4 parameters proved to be significantly different from zero in the optimized ppLFER fit. For comparison, a forward stepwise multiple linear regression analysis yielded the same significant terms and coefficients (Supplemental Data, Table S3).

RESULTS

Sorption kinetics.

Sorption time courses were assessed using toluene, which has a similar aqueous diffusivity (*ca*. 10^{-5} cm^2 s^{-1}) as our other probe sorbates. Dissolved toluene concentrations approached equilibrium in less than 1 week (Supplemental Data, Figure S1), and thus, we concluded that our incubation timeframe should be at least 1 wk to establish equilibrium, while at the same time not suffering losses during the incubations (e.g., since bubbles appeared). More sorptive probe compounds, such as pyrene or polychlorinated biphenyls, experience even greater retardation of diffusive transport into

183 porous char. Thus, they require longer equilibration times and are not yet included in this
184 set of probe compounds.
185
186 *Sorption isotherms.*
187 The Freundlich equation (Eqn. 1) fit the data for each sorbate well, with
188 correlation coefficients of at least 0.96, except for heptane (R^2 = 0.77) and diisopropyl
189 ether (R^2 = 0.87; Figure 2 and Table 2). Each isotherm was constructed using at least
190 eight data points, except for 1-heptanol (N=6). Within each compound class (e.g.,
191 alkanes, ethers, and alcohols), sorbates with the highest aqueous solubility exhibited the
192 lowest affinity for char (lowest sorption), except for diethylether (Figure 2). For alkanes,
193 alcohols, and ketones, the seven-carbon sorbate always had a larger K_f than the respective
194 six-carbon compounds (Table 2), likely reflecting their increased van der Waals
195 interactions with the char surface and increased cost of cavity formation in water due to
196 the addition of methylene groups. Although diethyl ether was the most soluble ether,
197 implying greater relative affinity for the solution phase, its larger K_f value compared to
198 MTBE and diisopropyl ether suggested intermolecular interactions with the char that
199 were not applicable to the branched ethers, such as due to steric effects.
200
201 *Polyparameter linear free energy relationships.*
202 To capture the saturation-dependent behavior of sorption, we fit the expanded
203 LFER expression (Eqn. 3), which includes a dependence on aqueous saturation (a =
204 $C_w/C_{w,sat}$), noting that aqueous saturation and sorption saturation must occur together in
205 our experiment if we successfully achieved equilibration. Using the 128 independent

206 $K_{d,activity}$ observations (Figure 3), we optimized the fit via the multiple regression statistic
207 F and found
208
209 $\log K_{d,activity}\,(\mathrm{L/kg}) = [(4.03 \pm 0.14) + (-0.15 \pm 0.04) \log a)]V$
210
211 $+ [(-0.28 \pm 0.04) \log a)]S + (-5.20 \pm 0.21)B$,
212
213 $R^2 = 0.98$, N=128, SE=0.41 (4)
214
215 For our data set, the coefficients for the *A* (hydrogen acidity/electron accepting capacity)
216 and *E* (molar refraction/polarizability) terms were not significantly different from zero,
217 suggesting these parameters did not substantially influence char-water sorption. Note
218 that the tested range of A was comparatively small (0 to 0.37), and dependence on A may
219 emerge if the data set were expanded. Further, the ppLFER should only be employed for
220 sorbates whose Abraham/McGowan parameters fall within the tested parameter space
221 (Table 1). Char-water partitioning depended directly on the dispersion interactions (*V*
222 term), inversely on the electron donating character (*B* term), and weakly on the sorbate's
223 polarizability (*S* term). Interestingly, the *V* term exhibited some dependence on
224 saturation, becoming more important at higher dilution; the *B* term did not exhibit
225 significant dependence on saturation over the investigated range, and the *S* term was only
226 important at low activities (e.g., $a<0.001$). The physical-chemical implications of these
227 dependencies are discussed below.
228

DISCUSSION

Consistency of ppLFER with previous observations.

Due to the prevalent use of activated carbon in water remediation applications, several research groups have previously developed activated carbon-water partitioning LFERs for organic compounds. While the exact coefficients differ (Table 3) [32-36], likely due to differences in GAC character and perhaps some experimental problems associated with assuming equilibrium before it is reached (Supplemental Data, Table S2), the important sorbate parameters are consistent: the molar volume (*V*) and electron-donation basicity (*B*) always exhibit the largest influence on the distribution coefficient, K_d. The dispersion term (*V*) always encourages sorption and the electron-donating basicity (*B*) of a sorbate always reduced sorption, and both were clearly different from zero.

The positive coefficient on the *V* term (Eqn. 4) largely results from the favorable free energy change associated from moving out of water to a hydrophobic surface. The activity dependency suggests more complete sorbate removal at low saturations (increasing influence of *V* term at low surface coverage), consistent with the view that the most favorable sorption sites involve deeper sorbate penetration into the porous char.

The negative impact of the *B* term implies that loss of hydrogen-bond donating interactions between the sorbate and solvent water are not replaced by interactions with the water-wet char. This is consistent with the expectation that aromatic pi electrons in the char can donate electron density to a hydrogen-bonding sorbate but cannot accept electron density from electron-donating sorbates [37]. The absence of aqueous saturation

dependence of the *B* term for char sorption suggests that this effect is independent of the surface coverage on the char. In other words, the saturation independent character and negative coefficient of B may simply reflect a constant "penalty" of sorbate removal from water, irrespective of sorbate position within the char.

Other terms made smaller contributions to K_d, as was observed for activated carbon (see Table 3). In the case of the wood char, the contribution of the polarizability parameter (*S*) to K_d was weak but activity dependent, becoming more positive at lower sorbate coverage. This may imply that dipole-induced dipole or dipole-dipole interactions with char are stronger at lower char surface coverages. At higher degrees of saturation, the dipole-induced dipole and dipole-dipole interactions with water and water-wet char may be roughly equivalent, and thus, the effect of the S term decreases in significance.

Interpretation of Freundlich parameters.

The Freundlich isotherm parameters K_f and n are influenced by a sorbate's structural parameters, and the ppLFER's dependence on chemical aqueous saturation allowed us to investigate this relationship. The distribution coefficient, K_d, is equal to C_s/C_w, and chemical activity, a, expresses the saturation level, $C_w/C_{w,sat}$; substituting these ratios into Equation 4 and rearranging yields

$$\log C_s = (4.03V - 5.20B) + (0.15V + 0.28S) \log C_{w,sat} + (-0.15V - 0.28S + 1) \log C_w \quad (5)$$

This equation (Eqn. 5) has the form of the log-transformed Freundlich isotherm expression (Eqn. 1), $\log C_s = \log K_f + n \log C_w$, and can thus be solved to determine log K_f and n in terms of the sorbate parameters, V, S, and B.

$$\log K_f\,[(\text{mg/kg})/(\text{mg/L})^n] = (4.03V - 5.20B) + (0.15V + 0.28S) \log C_{w,sat} \quad (6)$$

and

$$n = -0.15V - 0.28S + 1 \quad (7)$$

The accuracy of this approach is suggested by the goodness of fit of the observed data with those predicted by Equations 6 and 7 (Figure 4). As was observed for granular activated carbon (GAC) [32], the V and B terms are also the major contributors to the Freundlich coefficient observed for char. Dispersive forces (captured by the V term) encourage sorption and increase K_f, whereas electron donation capacity (reflected by the B term) decreases K_f. A sorbate's polarizability (S term) makes a minor contribution to the Freundlich coefficient and that contribution is higher for solutes with larger aqueous solubilities. For example, a typical hydrogen-bond accepting sorbate could have $V \approx 1$, $B \approx 0.5$, $S \approx 0.5$, and $\log C_{w,sat} \approx \log (1\ \text{mg/L}) = 1$, and thus, $\log K_f \approx 4.18 - 0.26 + 0.14 \approx 4$, where the terms correspond to the contributions of V, B, and S, respectively. In contrast, sorbates with little electron donating basicity and polarizability (i.e., B≈0 and S≈0) have

297 Freundlich coefficients almost entirely dependent on dispersive forces (the *V* term). This
298 is, perhaps, unsurprising and is consistent with observations.

299 The Freundlich exponent, *n*, captures the non-linearity of the sorption process,
300 and, in the case of sorption from water to water-wet char, this exponent exhibited a
301 dependence on dispersive forces and polarity (i.e., the *V* and *S* terms, respectively). Note
302 that the slope of the line is not significantly different from 1 (1.19 ± 0.36), indicating that
303 Equation 7 is capturing the right dependencies of *n* on sorbate properties, but the low R^2
304 (0.47) suggests the correlation does not perform with much precision). The *S* parameter
305 has been correlated with the Freundlich exponent in studies of sorption of organic
306 chemicals to peat soil and GAC [32, 38]. For GAC (Darco 20-40 mesh from Sigma-
307 Aldrich), Shih and Gschwend [32] noted that the electron donating basicity (*B* term)
308 made a small contribution to the Freundlich exponent, but this was not observed for our
309 char perhaps due to differences in the oxygen functionality of the materials. For nonpolar
310 compounds (e.g., with S≈0), the dispersive forces dominate the sorption behavior. For a
311 typical polar sorbate (e.g., with V≈1 and S≈0.5), the Freundlich exponent will have
312 roughly equal contributions from the dispersion and polarity terms, but these will be
313 dominated by the constant (+1). We note that the constant in the *n* expression for our
314 char (+1) was greater than seen previously for GAC (+0.76) [32]; this could imply that
315 the isotherm nonlinearity also has some dependency on sorbent properties (e.g., GAC vs.
316 wood char). For example, the exponent could capture the chemical nature of the char
317 surface and physical distribution of pore spaces. The Freundlich exponents for char were
318 systematically higher than those for GAC [32] (Supplemental Data, Table S2) and, as
319 noted earlier, could not be predicted by the same LFER. Knappe's group has

demonstrated that pore structure and surface composition (e.g., oxygen content) have a significant influence on the sorption behavior of organic chemicals [39,40], and differences in the physicochemical profile of the sorption surface may explain apparent differences in sorption properties of distinct BCs. Thus, sorbent-specific free energy relationships may be needed for distinct types of black carbon sorbent materials.

CONCLUSIONS

Overall, three primary lines of evidence support the results presented here and build confidence in this sorbent characterization approach: (1) the Freundlich parameters, K_f and n, individually make sense (e.g., polar compounds have n values closer to 1 and hydrophobic sorbates have larger K_f); (2) the ppLFER yielded four best-fit parameters (i.e., v_1, v_2, b_1, and s_2 in Eqns. 3 and 4) that were significantly different from zero from 128 individual observations; and (3) previous researchers have also observed positive relationships between K_d and V and negative relationships between K_d and B for similar forms of black carbon. Further, the fit also indicates that considering sorption as a function of the degree of surface saturation (where complete saturation is assumed to correspond to saturation in solution) yields a ppLFER that is understandable with respect to sorbate-sorbent interactions.

Moreover, our results support the hypothesis that two distinct types of black carbon, GAC and wood char, interact with organic sorbates *via* subtly different combinations of intermolecular interactions, which arise from the physical and chemical character of the respective sorbent materials. This implies a need for sorbent-specific

343 black-carbon distribution coefficients in order to predict contaminant distribution in
344 natural sediments or amended cleanup sites. Fortunately, we found that a relatively small
345 set of sorbate probe compounds can be used to generate a ppLFER that enables
346 estimation of BC-water distribution coefficients for sorbates of interest where sorption
347 data are unavailable (with the caution that the ppLFER should be used within the
348 investigated Abraham/McGowan parameter space (Table 1)). Further work needs to be
349 done to extend the tested parameter space, being sure to utilize sufficient incubation times
350 to insure solution-sorbent equilibration.

351 Furthermore, natural systems with more than one source of BC may require
352 quantification of each BC type to accurately predict contaminant distribution. While
353 independent measures to quantify distinct BC fractions are available, no single method
354 exists to differentiate all possible fractions of BC in environmental matrices. Such a
355 method would be useful if important chemical differences between BC types are
356 confirmed.

357

358 **SUPPLEMENTAL DATA**

359 Wood char characteristics, previously modeled black carbons and their sorbent
360 parameters, toluene equilibration timescale for water-wet char, and comparison of
361 Freundlich exponents between GAC and char.

362

363 **ACKNOWLEDGMENT**

364 The authors thank J. MacFarlane, M. Streng, Z. Henrot, and E. Forsley. This material is
365 based upon work supported by the U.S. Army Corps of Engineering, Humphreys

Engineer Center Support Activity under Contract No. W912HQ-10-C-0005 awarded as part of the SERDP program. The authors do not have any conflicts of interest to disclose.

REFERENCES

1. DiToro, D. M., C. Zarba, Hansen, D. J. , Berry, W. , Swartz, R. C., Cowan, C., Pavlou, S., Allen, H., Thomas, N., and Paquin, P. 1991. Technical basis for establishing sediment quality criteria for nonionic organic-chemicals using equilibrium partitioning. *Environmental Toxicology and Chemistry 10*, 1541.
2. Hawthorne, S.B., Grabanski, CB, Miller, DJ. 2006. Measured partitioning coefficients for parent and alkyl polycyclics aromatic hydrocarbons in 114 historically contaminated sediments: Part 1. K-OC values. *Environmental Toxicology and Chemistry* 25 (11): 2901-2911.
3. Hawthrone, SB, Grabanski, CB, Miller DJ. Measured partition coefficients for parent and alkyl polycyclic aromatic hydrocarbons in 114 historically contaminated sediments: part 2. Testing the k(oc)k(bc) two carbon-type model. 2007. *Environmental Toxicology and Chemistry* 26 (12): 2505-2516.
4. Fernandez, L.A., MacFarlane, J.K., Tcaciuc, A.P., Gschwend, P.M. 2009. Measurement of freely dissolved PAH concentrations in sediment beds using passive sampling with low density polyethylene strips. *Environ. Sci. & Technol*., *43*, 1430-1436.
5. Tracey, G.A., Hansen D.J. 1996. Use of biota-sediment accumulation factors to assess similarity of nonionic organic chemical exposure to benthically-coupled

388 organisms of differing trophic mode. *Arch. Environ. Contam. Tox. 30*, 467-
389 475.
390 6. Hellou, J., Steller, S., Zitko, V., Leonard, J., King, T., Milligan, T.G., Yeats, P.
391 2002. Partitioning of polycyclic aromatic hydrocarbons between water and
392 particles compared to bioaccumulation in mussels: a harbour case. *Mar. Env.*
393 *Res. 53*, 357-379.
394 7. Kraaij, R.H., Tolls, J., Sijm, D., Cornelissen, G., Heikens, A., Belfroid, A.
395 2002. Effects of contact time on the sequestration and bioavailability of
396 different classes of hydrophobic organic chemicals to benthid oligochaetes
397 (Tubificidae). *Environmental Toxicology and Chemistry 21*(4), 752-759.
398 8. Gustafsson, O., Haghseta, F., Chan, C., MacFarlane, J.K., Gschwend, P.M.
399 1997. Quantification of the dilute sedimentary soot phase: Implications for
400 PAH speciation and bioavailability. *Environ. Sci. Technol. 31*(1), 203-209.
401 9. Ghosh, U., Gillette, J.S., Luthy, R.G., Zare, R.N. 2000. Microscale location,
402 characterization, and association of polycyclic aromatic hydrocarbons on
403 harbor sediment particles. *Environ. Sci. Technol. 34*, 1729-1736.
404 10. Accardi-Dey, A., Gschwend P.M. 2002. Assessing the combined roles of
405 natural organic matter and black carbon as sorbents in sediments. *Environ. Sci.*
406 *Technol. 36*, 21-29.
407 11. Accardi-Dey, A., Gschwend P.M. 2003. Reinterpreting literature sorption data
408 considering both absorption into organic carbon and adsorption onto black
409 carbon. *Environ. Sci. Technol. 37*, 99-106.

410 12. Ghosh, U., Zimmerman, J.R., Luthy, R.G. 2003. PCB and PAH speciation
411 among particle types in contaminated sediments and effects on PAH
412 bioavailability. *Environ. Sci. Technol. 37*, 2209-2217.
413 13. Lohmann, R., MacFarlane, J.K., Gschwend, P.M. 2005. Importance of black
414 carbon to sorption of native PAHs, PCs, and PCDDs in Boston and New York
415 Harbor Sediments. *Environ. Sci. Technol.* 39, 141-148.
416 14. Ghosh, U., Talley, J.W., Luthy, R.G. 2011. Particle-Scale Investigation of PAH
417 Desorption Kinetics and Thermodynamics from Sediment. *Environ. Sci.*
418 *Technol. 35*, 3468-3475.
419 15. McBeath, A.V., Smernik, R.J., Krull, E.S. 2013. A demonstration of the high
420 variability of chars produced from wood in bushfires. *Organic Geochemistry*
421 *55*: 38-44.
422 16. Cao, X., Pignatello, J.J.; Li, Y.; Lattao, C.; Chappell, M.A., Chen, N.A., Miller,
423 L.F., Mao, J. 2012. Characterization of wood chars produced at different
424 temperatures using advanced solid-state ^{13}C NMR spectroscopic techniques.
425 *Energy & Fuels 26*, 5983-5991.
426 17. Lattao, C., Cao, X., Mao, J., Schmidt-Rohr, K., Pignatello, J.J. 2014. Influence
427 of molecular structure and adsorbent properties on sorption of organic
428 compounds to a temperature series of wood chars. *Environ. Sci. Technol. 48*,
429 4790-4796.
430 18. Goldberg, E.D. Black Carbon in the Environment, 1985, John Wiley, Hoboken,
431 N.J.

19. Baldock, J.A.; Smernik, R.J. 2002. Chemical composition and bioavailability of thermally altered *Pinus resiinosa* (Red pine) wood. *Org. Geochem. 33*, 1093-1109.

20. Chun, Y., Sheng, G., Chiou, C.T. 2004. Evaluation of current techniques for isolation of chars as natural adsorbents. *Environ. Sci. Technol. 38*, 4227-4232.

21. Hammes, K., Smernik, R.J., Skjemstad, J.O., Herzog, A., Vogt, U.F., Schmidt, M.W.I. 2006. Synthesis and characterization of laboratory-charred grass straw (Oryza sativa) and chestnut wood (Castanea sativa) as reference materials for black carbon quantification. *Organic Geochemistry 37*, 1629-1633.

22. European Environment Agency, Annual European Union Greenhouse Gas Inventory 1990-2012 and Inventory Report, Technical Report No. 9, Annex 2.9 CRF Tables LULUCF, European Union, 2014

23. Food and Agricultural Organization of the United Nations, Statistics Division (FAOSTAT), Biomass Burning, All, 1961-2011, Accessed in September 2014 via the World Wide Web.

24. Jaffe, R., Ding, Y., Niggemann, J., Vahatalo, A. V., Stubbins, A., Spencer, R. G. M., Campbell, J., Dittmar, T. 2013. Global charcoal mobilization from soils via dissolution and riverine transport to the oceans. *Science 340 (6130)*, 345–347.

25. Tulp, H.C., Goss, K-U, Schwarzenbach, R.P., Fenner, K. 2008. Experimental determination of LSER parameters for a set of 76 diverse pesticides and pharmaceuticals. *Environ. Sci. Technol. 42*, 2034-2040.

26. Zissimos, A. M., Abraham, M. H., Kamlet, A., Eclert, F., Wood, J. 2002. A

455 Comparison between the two general sets of linear free energy descriptors of
456 Abraham and Kamlet. *J. Chem. Inf. Comput. Sci. 42*: 1320-1331.
457 27. Elmquist, M., G. Cornelissen, Z. Kukulska, Gustafsson, Ö. 2006. Distinct
458 oxidative stabilities of char versus soot black carbon: Implications for
459 quantification and environmental recalcitrance. *Global Biogeochem. Cycles 20*,
460 GB2009, 11 pp.
461 28. Hammes, K., Schmidt, M.W. I., Smernik, R.J., Currie, L.A., Ball, W.P.,
462 Nguyen, T.H., Louchouarn, P., Houel, S., Gustafsson, Ö., Elmquist, M.,
463 Cornelissen, G., Skjemstad, J.O., Masiello, C.A., Song, J., Peng, P., Mitra, S.,
464 Dunn, J.C., Hatcher, P.G., Hockaday, W.C., Smith, D.M., Hartkopf-Fröder, C.,
465 Böhmer, A., Lüer, B., Huebert, B.J., Amelung, W., Brodowski, S., Huang, L.,
466 Zhang, W., Gschwend, P.M., Flores-Cervantes, D.X., Largeau, C., Rouzaud,
467 J.-N., Rumpel, C, Guggenberger, G., Kaiser, K., Rodionov, A., Gonzalez-Vila,
468 F.J., Gonzalez-Perez, J.A., de la Rosa, J.M., Manning, D.A.C., López-Capél, E.,
469 Ding. L. 2007. Comparison of quantification methods to measure fire-derived
470 (black/elemental) carbon in soils and sediments using reference materials from
471 soil, water, sediment and the atmosphere. *Global Biogeochem. Cycles 21* (3):
472 Art. No. GB3016, 18 pp.
473 29. Lion, L. W., Stauffer, T. B., MacIntyre, W. G. 1990. Sorption of hydrophobic
474 compounds on aquifer materials: Analysis methods and the effect of organic
475 carbon. *J. Contam. Hydrol. 5*, 215-234.
476 30. Goss, K.-U., Schwarzenbach, R. P. 1998. Gas/solid and gas/liquid partitioning
477 of organic compounds: critical evaluation of the interpretation of equilibrium

478 constants. *Environ. Sci. Technol. 32*, 2025-2032.

479 31. Lung, S. C., Altshul, L. M., Ford, T. E., Spefngler, J. D. 2000. Coating effects
480 on the glass adsorption of polychlorinated biphenyl (PCB) congeners.
481 *Chemosphere 41*,1865–1873.

482 32. Kamlet, M. J., Doherty, R. M., Abraham, M H., Taft, R. 1985. Linear solvation
483 energy relationships. XXXIII: An analysis of the factors that influence
484 adsorption of organic compounds on activated carbon. *Carbon 23*, 549-554.

485 33. Luehrs, D.C., Hickey, J.P., Nilsen, P.E., Godbole, K.A., Rogers, T.N. 1996a.
486 Linear solvation energy relationship of the limiting partition coefficient of
487 organic solutes between water and activated carbon. *Environ. Sci. Technol. 30*,
488 143-152.

489 34. Luehrs, D.C., Hickey, J.P., Passino-Reader, D.R. 1996b. Linear solvation
490 energy relationships: “Rule of thubs” for estimation of variable values. *Environ.*
491 *Sci. Technol. 30*, 143-152.

492 35. Poole, S. K., Poole, C. F. 1997. Retention of neutral organic compounds from
493 solution on carbon adsorbents. *Anal. Commun*. *34*, 247-251.

494 36. Shih, Y.-H., Gschwend, P.M. 2009. Evaluating activated carbon-water sorption
495 coefficients of organic compounds using a linear solvation energy relationship
496 (LSER) approach and sorbate chemical activities. *Environ. Sci. Technol. 43*,
497 851-857.

498 37. Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M. 2003. *Environmental*
499 *Organic Chemistry*, 2nd Edition, Wiley-Interscience, New York, N.Y.

500 38. Endo, S., Grathwohl, P., Haderlein, S. B., Schmidt, T. C. 2008. Compound-

specific factors influencing sorption nonlineariry in natural organic matter. *Environ. Sci. Technol. 42*, 5897-5903.

39. Li L, Quinlivan, P. A., Knappe, D. R. U. 2002. Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution. *Carbon 40*, 2085-2100.

40. Li L, Quinlivan, P. A., Knappe, D. R. U. 2005. Predicting adsorption isotherms for aqueous organic micropollutants from activated carbon and pollutant properties. *Environ. Sci. Technol. 39*, 3393 -3400.

FIGURE LEGENDS

Figure 1. Dominant sources of biochar and illustrated pore and surface structures. Biochar is a ubiquitous sorbate that has natural, incidental, and engineered sources. The arrow thicknesses indicate the postulated relative sizes of the predominant source terms [22-24]. Biochars are formed from the incomplete combustion of biological material, such as wood, leaves, husks, and grasses, and often have microstructures that reflect the structure of the original biological material. (Wood char is depicted here). On the molecular scale, biochar is characterized by a highly aromatic surface with some oxygen content and can interact with sorbents, such as nitrobenzene, via electron donator-acceptor and van der Waals interactions.

Figure 2. Freundlich isotherms for 14 probe sorbates on chestnut wood char. Solid and dashed lines are best-fit curves, from which we derive characteristic Freundlich parameters, log K_f (intercept) and n (slope). See Table 2 for parameter values.

Figure 3. Overall correlation of the individual observed sorption coefficients with the predicted sorption coefficients. Predicted values were determined using the ppLFER given by Equation 4, whereas the observations were experimentally determined from the 128 individual equilibrium experiments conducted in the present study.

Figure 4. Correlations of observed Freundlich coefficients, K_f [(mg/kg)/(mg/L)^n], and the Freundlich exponent, n, with ppLFER-predicted values for those parameters. Predicted values were determined using Equations 6 and 7. Diagonal dashed lines are the

533 one-to-one lines, while solid lines are linear best fits. Error bars represent one standard

534 deviation; invisible error bars are smaller than the symbol.